

# Needs of In-Situ Synchrotron Techniques for Non-Pt Catalysts

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# Motivation for Non-Pt Catalysis

Bulk Metal Prices in the United States in 9/2005

	Pt	W	Ti	V	Cr	Mn	Fe	Co	Ni
Price (\$/kg)	29,200	1.10	24.00	45.20	1.36	0.52	0.50	39.00	13.82

[www.metalprices.com](http://www.metalprices.com)

Potential advantages of bimetallic and carbide catalysts:

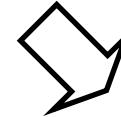
- Reduce cost
- Enhance activity and selectivity

# Bimetallic and Carbide Catalysts

<i>Ti</i>	<i>V</i>	<i>Cr</i>	<i>Mn</i>	<i>Fe</i>	<i>Co</i>	<i>Ni</i>	<i>Cu</i>
<i>Zr</i>	<i>Nb</i>	<i>Mo</i>	<i>Tc</i>	<i>Ru</i>	<i>Rh</i>	<i>Pd</i>	<i>Ag</i>
<i>Hf</i>	<i>Ta</i>	<i>W</i>	<i>Re</i>	<i>Os</i>	<i>Ir</i>	<i>Pt</i>	<i>Au</i>



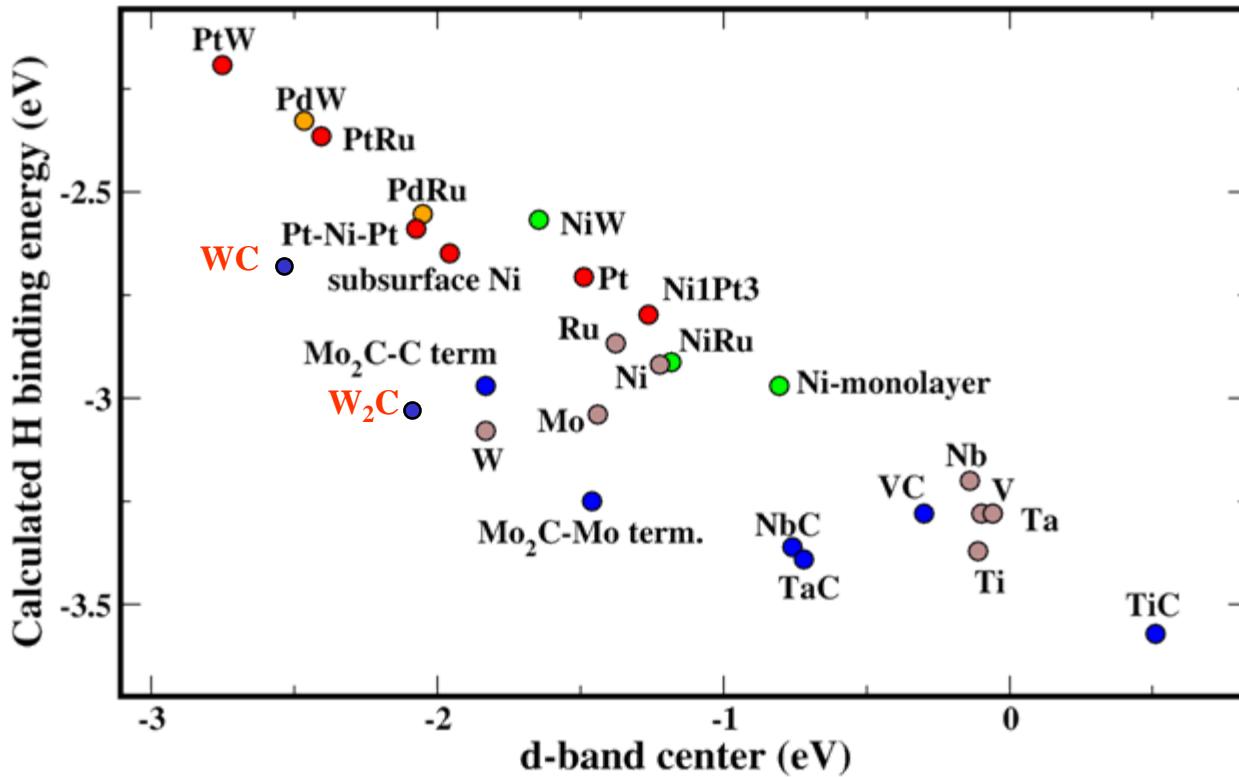
Metal carbides



Pt-metal alloys

- Chemical/electronic properties are often tunable:
  - alloying with carbon -> **non-Pt carbides**
  - alloying with another metal -> **Pt-3d alloys**

# DFT of Surface d-Band Center of Carbide and Bimetallic Catalysts:



Controlling properties of carbide and bimetallic surfaces:

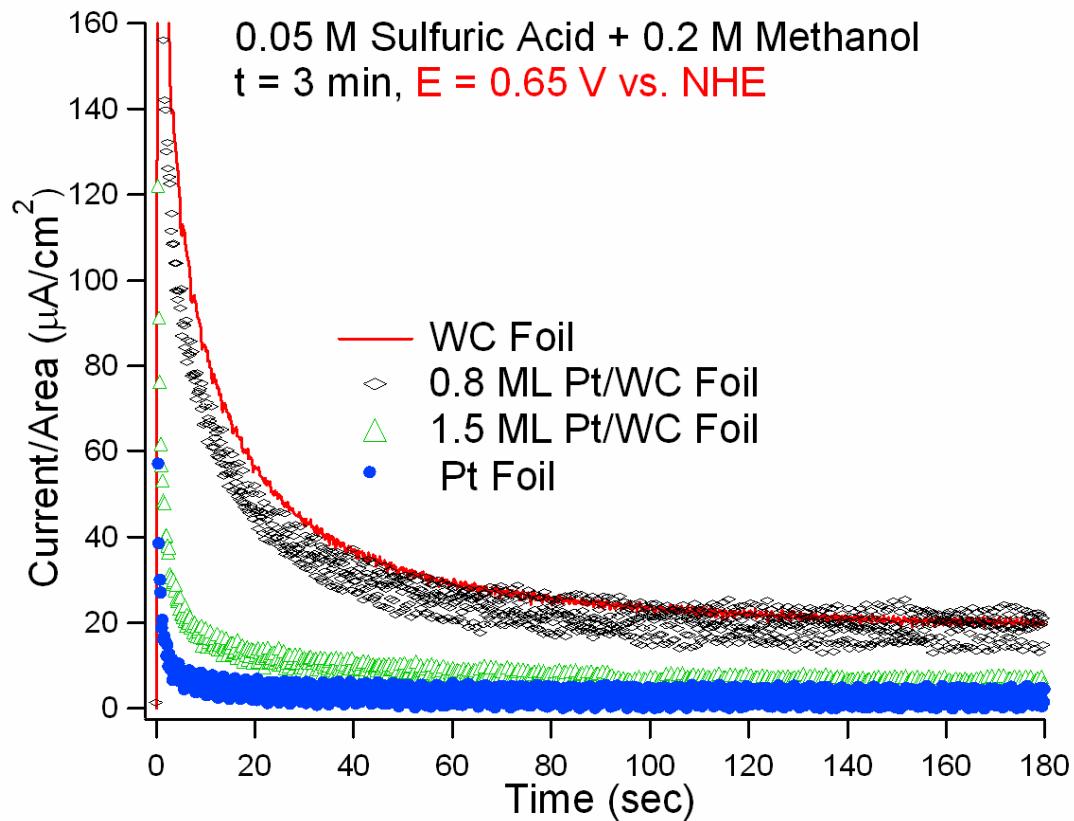
Kitchin et al. Phys. Rev. Lett. 93 (2004) 156801

Kitchin et al. Catal. Today 105 (2005) 66

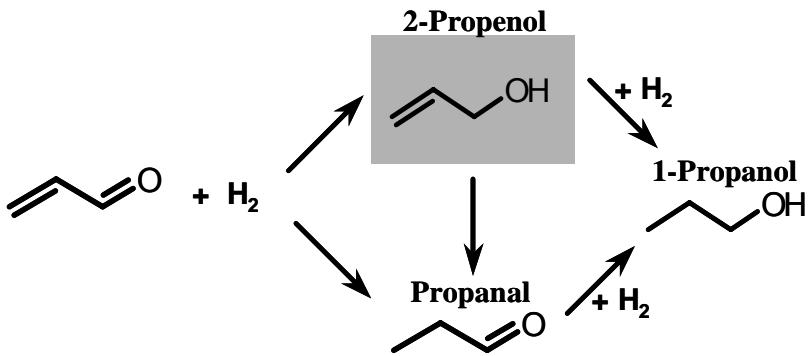
Liu et al. in preparation

# Chronoamperometry (CA) of WC and Pt/WC as Electrocatalysts for Fuel Cells

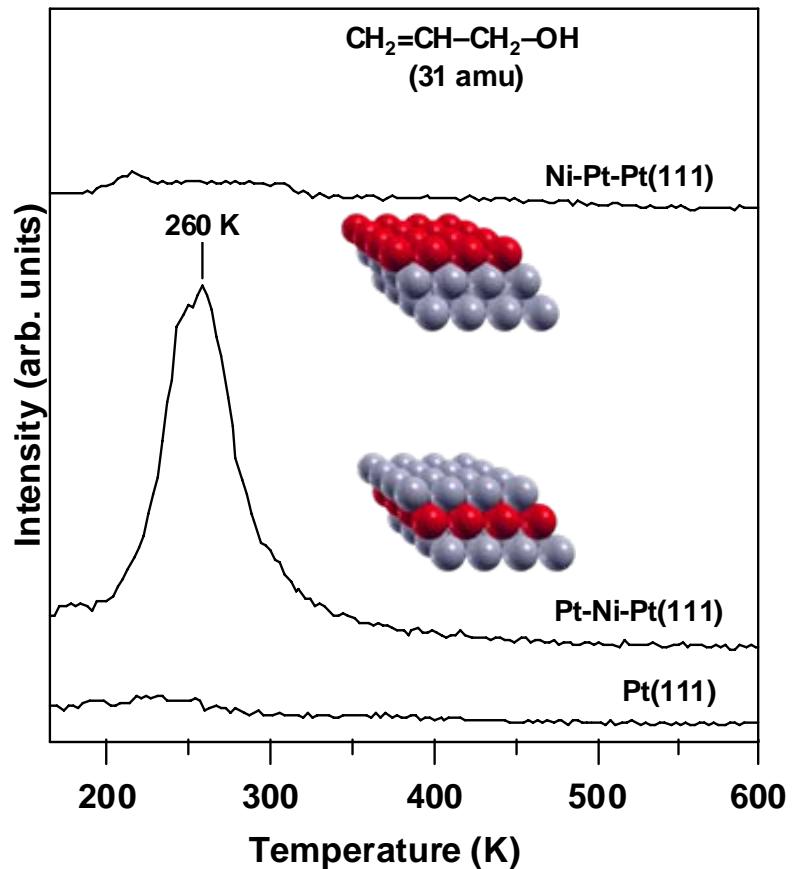
- Steady-state current of WC and 0.8 ML Pt/WC higher than Pt
- **Needs in-situ study of active phases and stability of WC under fuel cell conditions**



# Novel Hydrogenation Properties of Bimetallic Surfaces



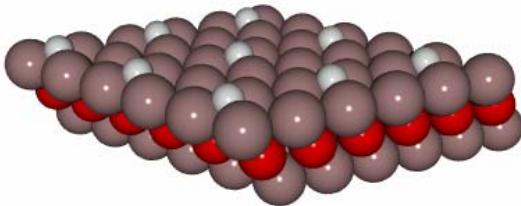
Selective hydrogenation of C=O bond only occurs on subsurface Pt-Ni-Pt(111)



# Stability of Bimetallic Surfaces under Reaction Conditions

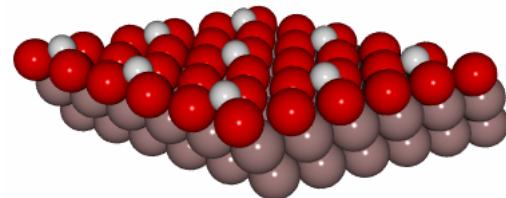
d-band center away  
from Fermi level:

- Hydrogenation
- $O_2$  reduction



d-band center closer  
to Fermi level:

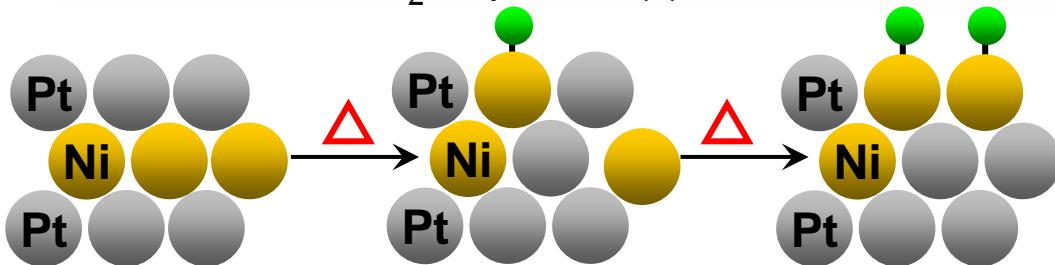
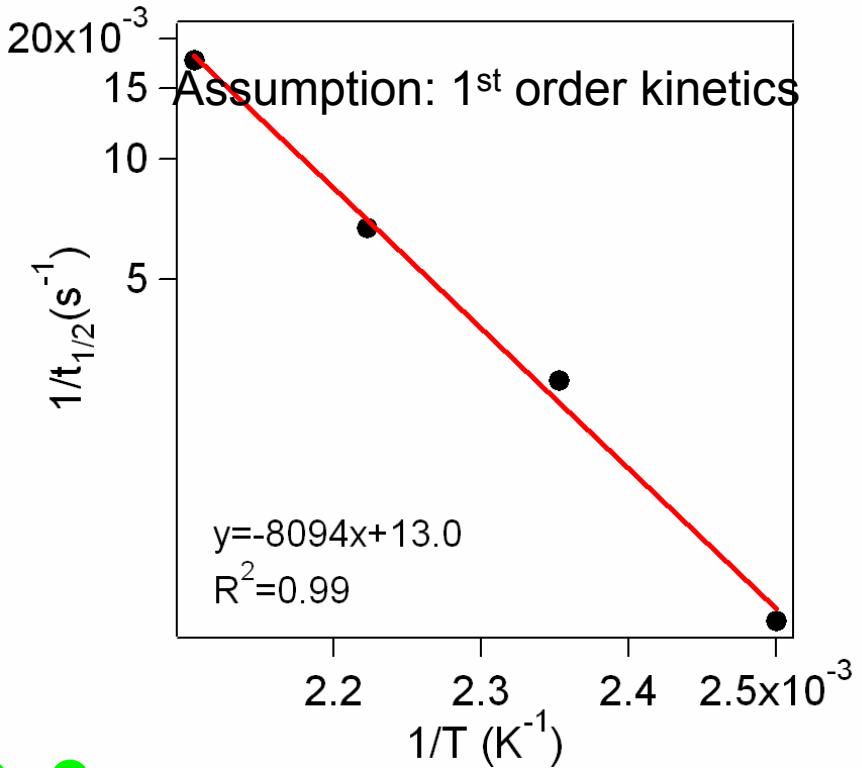
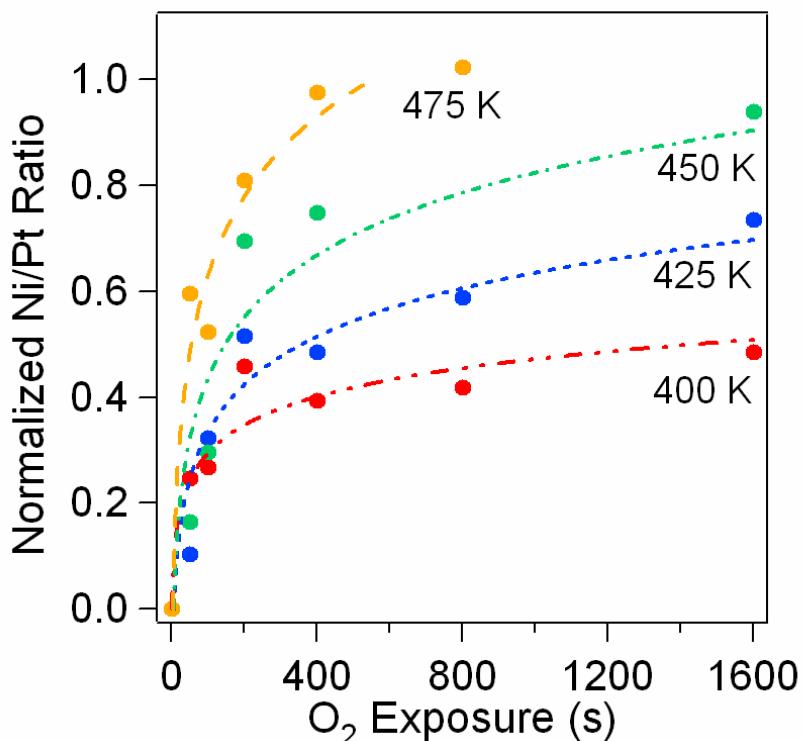
- Reforming reaction
- Dehydrogenation



Chen, Menning, Zellner, Surf. Sci. Reports (2008)

*Critical Needs: in-situ technique to determine  
stability of bimetallic structures*

# Experimental Verification: Segregation of Ni in Pt-Ni-Pt(111)



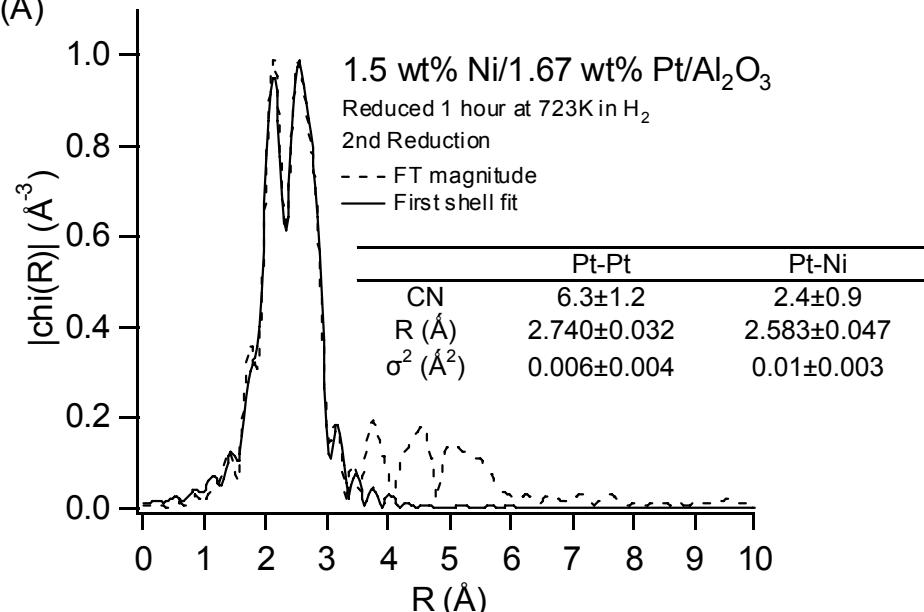
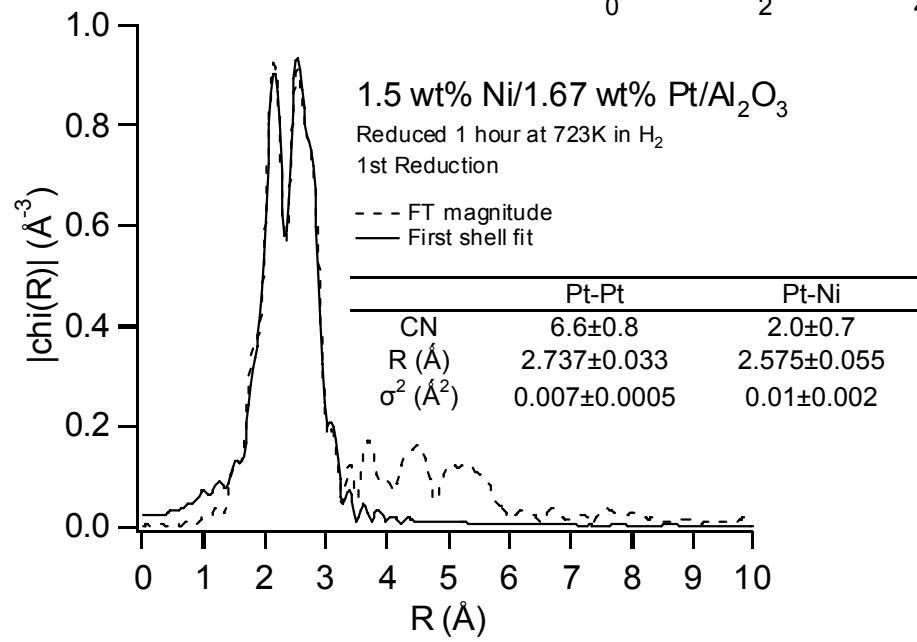
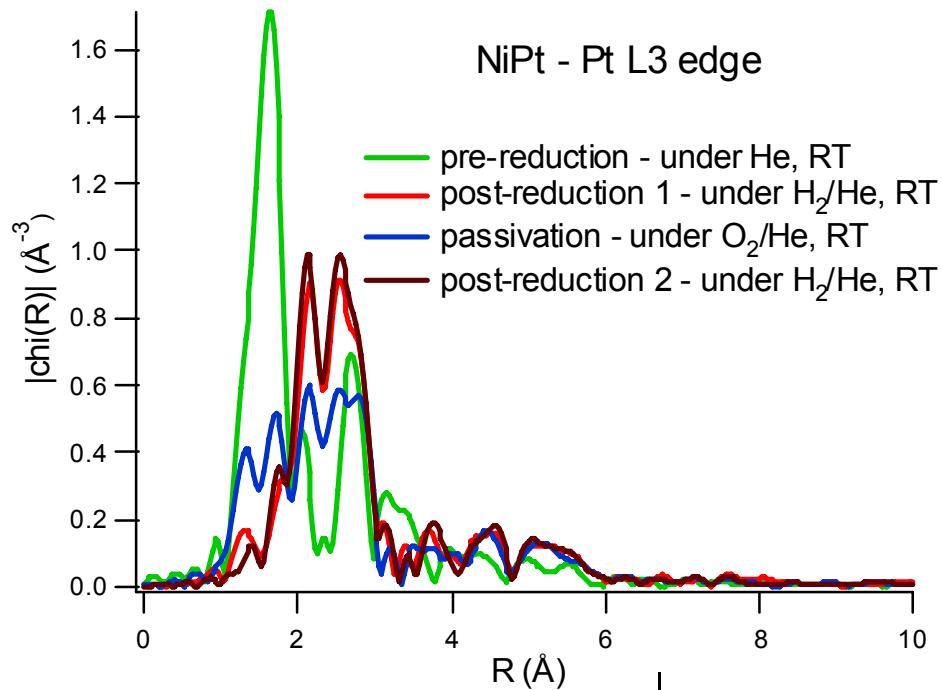
$$E_a = 15 \pm 2 \text{ kcal/mol}$$

for Pt-Ni-Pt(111)

$$E_a = 7 \pm 1 \text{ kcal/mol}$$

for Pt-Co-Pt(111)

# EXAFS of Supported Ni/Pt/Al<sub>2</sub>O<sub>3</sub> (3:1 Ni:Pt)



# **Needs of In-Situ Synchrotron Techniques for Non-Pt Catalysts**

- Carbide catalysts
  - Active phase (carbides, oxycarbides?)
  - Stability (degree of oxidation?)
- Bimetallic catalysts
  - Bimetallic structures (surface, subsurface, mixed?)
  - Stability (segregation of metal components?)